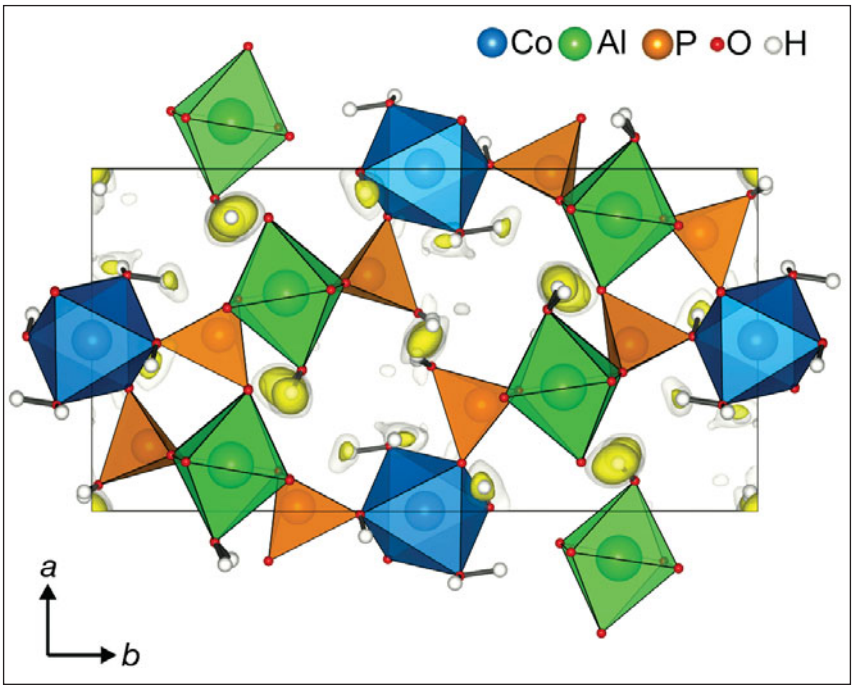
Nano Focus

Electron diffraction enables localization of hydrogen atoms in nanocrystals

It has not been possible thus far to use diffraction methods, such as x-ray diffraction, to localize the precise locations of hydrogen atoms in nano-sized crystals due to their strong atomic vibrations and small scattering cross sections.

An international team of researchers from the Institute of Physics of The Czech Academy of Sciences, Laboratoire de Cristallographie et Sciences des Matériaux (CRISMAT), and Laboratoire Catalyse et Spectrochimie has now developed a method to locate hydrogen atoms within submicrometer crystals. As reported in a recent issue of *Science* (doi:10.1126/science.aak9652), this was achieved using the recently developed method of dynamical refinement of precession electron diffraction tomography data.

"We followed standard crystallographic routine to collect a complete diffraction data set, then localized the heavy atoms (i.e., all non-hydrogen atoms) by *ab initio* methods and further refined using our dynamical refinement method," says Lukáš Palatinus from The Czech Academy of Sciences and lead author. "The key ingredient in this procedure is the dynamical refinement method, which enables us to calculate the diffracted intensities and the difference potential map. This allows the localization of hydrogen atoms, which are found at the maxima in the difference potential map," adds co-author Philippe Boullay of CRISMAT.



Projection of cobalt aluminophosphate crystal structure with superimposed difference potential map. Hydrogen positions are located by finding the local maxima of this potential map. Credit: *Science*.

"The dynamical refinement method developed by Palatinus et al. features an impressive enhancement in accurate determination of crystal structure by electron diffraction technique, with reduced discrepancies in atomic positions and more meaningful reliability factor," says Doug Perovic, an expert in scanning transmission electron microscopy and spectroscopy of nanomaterials structure and chemistry at the University of Toronto, who was not involved in this study. "The ability to localize the lightest atom-hydrogen is a clear demonstration of the capability of this method," he adds.

"We hope our work can attract newcomers in the field to develop, extend, and democratize the use of electron crystallography," Boullay says. In the future, the researchers plan to take their refinement method to the next stage by analyzing and improving remaining imperfections, and extending the scope of analysis to twinned crystals, for example.

Xiwen Gong

Size matters in mechanical behavior of bulk metallic glasses

Metallic glasses are amorphous materials produced by rapidly quenching metallic alloys, "locking" them into a glassy state rather than the crystalline structures into which metals typically form.

The unusual atomic structure of bulk metallic glasses (BMGs) affords ultrahigh yield and tensile strengths, low stiffness, and often a remarkable fracture resistance putting BMGs among the most damage-tolerant materials known. These desirable qualities make metallic glasses an interesting engineering materials system. Indeed, more than 50 years after their discovery, BMGs are now among the most promising candidates for use in consumer electronics frames and casings, cardiovascular stents, and precision surgical instruments.

However, BMGS are yet to gain widespread use due to the large variability in their mechanical performance: the unpredictable fracture and toughness behavior of this class of materials have compromised their potential use for many structural applications. As William L. Johnson, a prominent figure in these efforts, said in 2015 based on his experience in commercializing bulk metallic glasses for golf clubs, "it takes at least 15–20

years to turn a laboratory material into a successful commercial venture."

Testing conditions can strongly influence the mechanical behavior of metallic glasses. For example, in strength tests, BMGs typically show local strain-softening behavior in tension and compression with strain localization often occurring on a single shear band. However, in bending these materials can demonstrate some strain hardening as a result of the geometrical loading conditions that lead to the formation and multiplication of shear bands. Furthermore, fatigue properties can display a particularly high susceptibility to the testing environment, affecting their fatigue strengths and crack-growth behavior.

Based on their recent work understanding variations in the properties of BMGs, scientists at Lawrence Berkeley National Laboratory, University of California, Berkeley, and ETH Zürich examined the variation in fracture toughness of the palladium-based metallic glass $Pd_{77.5}Cu_6Si_{16.5}$. Led by Bernd Gludovatz and Robert O. Ritchie, the team studied the material in a highly constrained single-edge notched bend geometry in two different sizes: one significantly smaller than, and another comparable to, the critical bending thickness—which is the critical dimension below which the number of shear bands needed to demonstrate significant ductility when subjected to bending is achieved. The resultant fracture toughness and fracture behavior were compared with ASTM-recommended sample geometries and size configurations.

As reported in a recent issue of *Acta Materialia* (doi:10.1016/j.actamat.2016.12.054), the research team found marked differences between the toughness values and failure characteristics of the two samples. The larger samples showed significantly larger variations in toughness values—and all essentially failed catastrophically—while none of the smaller samples failed catastrophically, yet displayed far less scatter in their measured toughness.

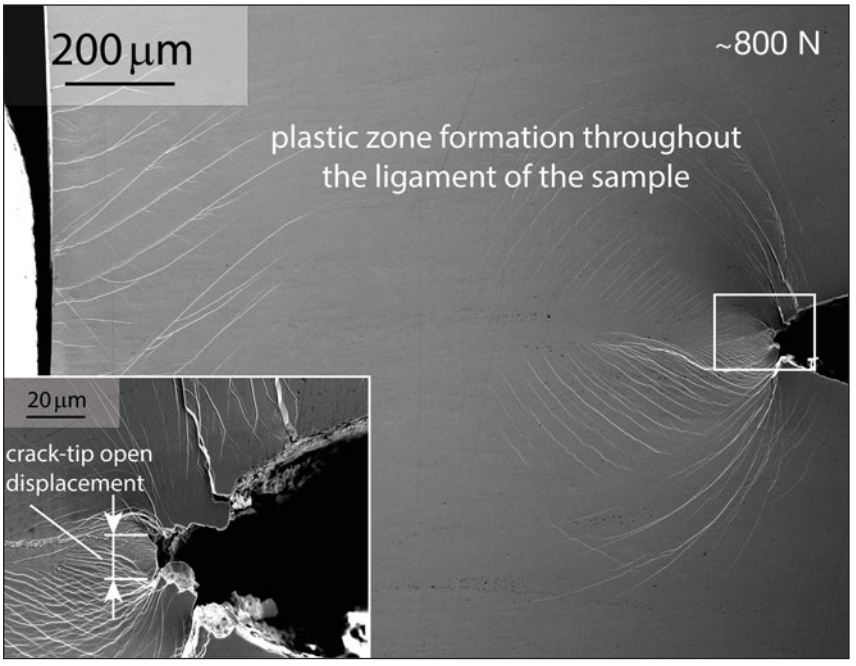
To gain further insight, *in situ* tests were carried out in a scanning electron microscope. These revealed that metallic glasses show a transition in fracture behavior that is linked to their sample size. Samples with ligament widths—that is, the dimension from the root of a pre-cracked notch to the back of the sample—larger than the critical bending thickness of the material demonstrated brittle failure characteristics and low fracture toughness values with only small variations. In contrast, samples with dimensions comparable to the critical bending thickness yielded highly variable, size- and geometry-dependent fracture toughness results.

"Based on the findings of this study, it is apparent that the reliable measurement of the toughness of metallic glasses presents a considerable challenge. These materials clearly can display quite brittle behavior in appropriately large sections yet distinctly different fracture properties in much thinner sections," Ritchie says. "These insights may help us unlock the technological promise of BMGs and the scientific underpinnings of their complex metallic glass behavior."

In general, the team's findings suggest that the fracture toughness measured for metallic glass samples tested with ligament widths either comparable or below the critical bending thickness should be considered size- and geometry-dependent. A ligament and thickness dimension exceeding the critical bending thickness is mandatory to determine a size- and geometry-independent fracture toughness of a metallic glass.

"This is a meaningful beginning for revealing the real fracture behavior of metallic glasses," says K.-F. Yao of Tsinghua University, who was not involved in this research. "Additional studies will help our community fully understand the exact effects of size and geometry in determining precisely the fracture toughness values of BMGs, which is based on the many factors affecting their fracture behavior such as sample size and shape, notch radius, fatigue crack, loading condition, and measuring method."

Aditi Risbud



Evolution of failure in the *in situ* tested small $Pd_{77.5}Cu_6Si_{16.5}$ sample. The onset of shear-band formation for the pre-cracked sample occurred around ~200 N before shear bands formed both in the back of the sample and from the root of the razor-notch at a load of ~800 N, leading to pronounced crack-tip opening displacement as shown in this figure. Credit: Bernd Gludovatz, Lawrence Berkeley National Laboratory.